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SPECTRAL CHARACTERISTICS OF FLARES  
CONTAINING SODIUM IODATE AS AN  
OXIDIZER

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Crane, Indiana

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  Spectra are presented for several flare formulations which incorporated sodium iodate as the oxidizer and magnesium as the fuel. While the flares containing iodate did not produce increased candlepower, several new spectral features were observed. One of the most interesting features was increased emission in the blue region of the spectrum over that obtained from the typical magnesium-sodium nitrate formulations. This emission is attributed to the recombination of iodine atoms in the $^3\Pi_0+u$ electronic		

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state of molecular iodine followed by emission from this state. Other emission features are discussed. Color measurements indicate that the iodate flares are more "white" possibly making them better for target acquisition than sodium nitrate flares.

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## INTRODUCTION

Obtaining high light output efficiency from pyrotechnic devices has always been a major problem and it would be a tremendous advantage if the efficiency could be improved substantially.

Light output from the chemical reactions in flares originates by atoms or molecules in an excited state dropping to the ground state, emitting radiation. Traditional pyrotechnic reactions produce species in their ground state. Some of these species are then excited to an upper electronic state by a purely thermal mechanism. Thermal excitation, however, is a very inefficient method of producing excited species.

If the emitting species in a pyrotechnic reaction could be formed directly in an excited state, the efficiency could be greatly improved. If the excited state molecule can also be chosen to emit in specific wavelength regions, the regions of interest would be from 430-570 nm, i.e. that region where sodium does not emit strongly.

Arnold, Finlayson and Ogryzlo discovered an intense iodine chemiluminescence in the yellow region of the spectrum and attributed it to iodine atom recombination.<sup>1</sup> As far as can be determined, iodine compounds have not been considered for illuminating compositions.<sup>2</sup>

## EXPERIMENTAL

In order to test the applicability of using sodium iodate as an oxidizer and to obtain specific emission from iodine, flares were made with the formulas shown in Table 1. Control flares composed of magnesium-sodium nitrate were also prepared. The flares were 33 mm in diameter, 25 mm long and contained 50 grams of composition. In addition, two grams of boron-barium chromate were pressed on the candles as a first fire.

The flares were burned face up at a distance of 400 cm from the measuring instruments. Relative luminous energy and burning times were monitored by recording the output of an EG&G Model 580 radiometer equipped with a photometric filter on an x-y plotter. Table 2 contains a summary of the relative powers and burning times.

To prevent confusion over actual candlepower values which would obviously be different for these small diameter flares when compared with full size illuminating flares, the data are all normalized relative to the fuel-rich magnesium-sodium nitrate formulation, Group 104.

At the same time that the power measurements were made, spectra were taken in the visible region from 380 nm - 680 nm. The spectra were taken on a Bausch and Lomb 1.5-m grating spectrograph using Linagraph Shellburst film. The instrument is equipped with a 450 groove/mm grating blazed at 490 nm and has a dispersion of 15 Å/mm in the first order. The flare was masked in such a way that the light hitting the spectrometer was from the region of the flame approximately two flare diameters above the burning surface.

After each flare spectrum was taken, several spectra of a 200 watt quartz iodine lamp were taken on the same film. These spectra were used to correct the flare spectra for the film response.

In an effort to study the new emission features apparent in the sodium iodate flares, spectra were taken at higher resolution with a 1-m Spex grating spectrograph. This spectrograph is equipped with a 1200 g/mm grating blazed at 500 nm. To provide the higher resolution, spectra were taken in the second order over the limited wavelength region from 515-580 nm. The spectrograph dispersion in this region in the second order is 2.7 Å/mm. Kodak Tri-X glass plates were used for recording the spectra.

Microdensitometer traces of all spectra were made on an Optronics densitometer. For the low resolution results, digital readings of film density were recorded at 100 micron, i.e. 1.5 Å, intervals along the entire wavelength region. For the high resolution spectra, digital readings were recorded at 12.5 micron, i.e. 0.03 Å, in the wavelength region used. The density readings were converted to radiant power by applying the film correction function generated from the quartz-iodine lamp spectra. These spectra were then converted to luminous power spectra by multiplying the radiant power by the photopic luminous efficiency function, i.e. the eye response curve.

The resulting spectra normalized to a value of one at the maximum emission are shown in Figs. 1-11. Figure 11 is the high resolution spectra of Group 101 magnesium-sodium iodate.

## DISCUSSION

The compositions of the flare Groups 101 and 105 shown in Table 1 were chosen by adjusting the fuel to oxidizer ratio in the NASA thermodynamics program until the maximum flame temperature was found.<sup>4</sup> This optimum formula was used as a starting point for formulations. It is a known fact that fuel rich formulas tend to produce more light than the so-called optimum formula.<sup>5</sup> Thus, Groups 102 and 103 were arbitrarily selected as fuel-rich sodium iodate formulas. Group 104 is a fuel-rich formula similar to the current Mk 45 aircraft parachute flare formula.

The data presented in Table 2 clearly show that the use of sodium iodate as an oxidizer causes a decrease of about a factor of three in both candlepower and efficiency. This loss in output is probably a result of the reduction in the sodium atom concentration. Due to the high molecular weight of sodium iodate, the sodium concentration in Group 101 is 24% less than in Group 104. The reduction in concentration means that there are not only less sodium atoms to emit but it has been shown that a reduction in sodium atom concentration also causes a narrowing of the broadened sodium D resonance lines.<sup>6</sup> Sodium D emission accounts for most of the light output in magnesium-sodium nitrate illuminating flares. Fig. 12 shows a superposition of the spectra of the iodate containing flares and the nitrate containing flares. The half-width of the sodium D region in the nitrate flares is 400 Å while the half-width in the iodate is only 160 Å. The calculation of the resonance broadening using Doude's method and lowering the sodium atom density by 25% reduces the broadening to only 300 Å. In order to fit the data, it is necessary to adjust the Voigt  $\alpha$  parameter. A value of the Voigt  $\alpha$  parameter of 0.20 gives a good fit to the experimental data. Reducing the  $\alpha$  parameter is equivalent to reducing the broadening due to like and unlike species in the flame. The resonance broadening half-width, i.e. broadening of sodium resonance lines by sodium atoms, is reduced because there are fewer sodium atoms in the system. The collisional broadening half-width, i.e. broadening due to collisions between sodium and unlike species, is reduced due to the increased reduced mass of the system because of the added iodine. Order of magnitude calculations show that these reductions in half-widths are not entirely sufficient to account for the reduction in the  $\alpha$  parameter. A detailed treatment, however, to explain these differences is beyond the scope of this paper. Arguments can be made to show that the broadening and the  $\alpha$  parameter are very sensitive functions of temperature and concentration of species in the flame. The problem of

mapping temperature and concentration gradients in a pyrotechnic flame is at the present time very difficult. Much more experimental work in this area is necessary in order to resolve the fine points in a calculation such as the one done by Doua.

The decreased luminous output in the sodium iodate flares would tend to rule out the use of the iodate as an oxidizer. There are, however, interesting features in the spectra which should be pointed out for use in special applications where the high intensity of the magnesium-sodium nitrate formula is not necessary.

The two most striking features in the spectra of the magnesium-sodium iodate flares, see e.g. Fig. 2, are the strong band emission at 538 and 560 nm and the increased continuum in the blue region from 400 - 530 nm. In addition to those shown, there is band emission at 380 nm similar in size and shape to that at 538 and 560.

The observed blue continuum is assigned to the molecular iodine  $B^3\Pi_{0+u} \leftrightarrow X^1\Sigma_g^+$  transition.<sup>7</sup> Figure 13 shows the two potential energy surfaces responsible for this transition. There are two possible mechanisms for the production of this emission. The emitting iodine molecule is formed by recombination of iodine atoms.



In a thermal excitation model, the ground state iodine molecule formed by this reaction would be thermally excited to the upper electronic state which would then emit. Another mechanism would be for the iodine recombination reaction to form the excited state directly followed by the observed emission. Either of these two mechanisms is reasonable due to the high temperatures in the flame. Based on the results which have been obtained, it is impossible to distinguish between the two mechanisms. More detailed studies would be required to observe the molecular and the atomic iodine emission and absorption simultaneously. This type of information would be required to completely determine the reaction mechanism.

The band emissions at 380, 538 and 561 nm have been identified as barium iodide  $A^2\Pi \leftrightarrow X^2\Sigma$  transition.<sup>7</sup> Barium emission is also seen as atomic emission at 554 nm. The barium in the flare comes from the barium in the boron barium chromate first fire. The barium emission is seen throughout the entire burning time and not just at the start of the burn.

The spectra shown in Fig. 11 unfortunately was not sufficiently resolved to allow calculation of any molecular constants for BaI.

While the spectra were being taken, visual observations of the flares indicated that the sodium iodate flares appeared to be whiter in color than the sodium nitrate. In an effort to quantify this observation to some extent, the spectral information obtained on Group 101 and 104 flares, Figs. 2 and 10, was converted to the tristimulus color values X, Y and Z from which one can obtain the dominant wavelength and purity of each flare.<sup>3</sup> Fig. 14 shows a chromaticity diagram with the points marked for Groups 101 and 104. As can be seen, the iodate are rendered more nearly white than the sodium nitrate flares. For the iodate flares, the dominant wavelength is 583 nm and the purity is 81%. For the nitrate flares, the dominant wavelength is 584 nm and the purity is 94%. The fact that the sodium iodate flares are more nearly white is due to the increased emission in the blue region of the spectrum.

Although little work has been done in the area of the effect of color on target acquisition, it would seem that a source with a more uniform distribution of light would be preferable to a highly monochromatic source. Thus, if one were interested in white flare light of moderate intensity, the magnesium-sodium iodate composition would provide a reasonable system.

### CONCLUSIONS

Flares composed of magnesium and sodium iodate show increased emission in the blue region of the spectrum. While the total luminous power is a factor of three less in the iodate flares than in magnesium-sodium nitrate flares, the increased blue emission makes the output of the iodate flares appear whiter. The blue emission is assigned to the  $A \rightarrow X$  transition of molecular iodine.

Band systems due to barium iodide formed by the reaction of the iodine atoms with the barium first fire were identified. The systems at 538 and 561 nm were observed under moderate resolution to determine molecular constants. Due to a lack of resolution, this was not possible. The emission bands are very specific and seem to be reasonably strong based on the fact that they are due to a barium impurity.



Magnesium-sodium iodate flares could be used as a moderate intensity white light source for better target acquisition. The use of barium and iodine containing flares might provide increased specific emission at 538 and 560 nm.

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TABLE 1  
FLARE COMPOSITIONS

Ingredient	101	102	Group 103	104	105
Mg	28.5	38.5	48.5	58.0	44.0
NaIO <sub>4</sub>	67.0	57.0	47.0	--	--
NaNO <sub>3</sub>	--	--	--	37.5	51.5
Binder	4.5	4.5	4.5	4.5	4.5

TABLE 2  
RELATIVE POWERS AND BURN TIMES

Group	Relative Power	Burn Time
101	0.17	20 sec.
102	0.32	26 sec.
103	0.28	28 sec.
104	1.00	23 sec.
105	0.93	25 sec.

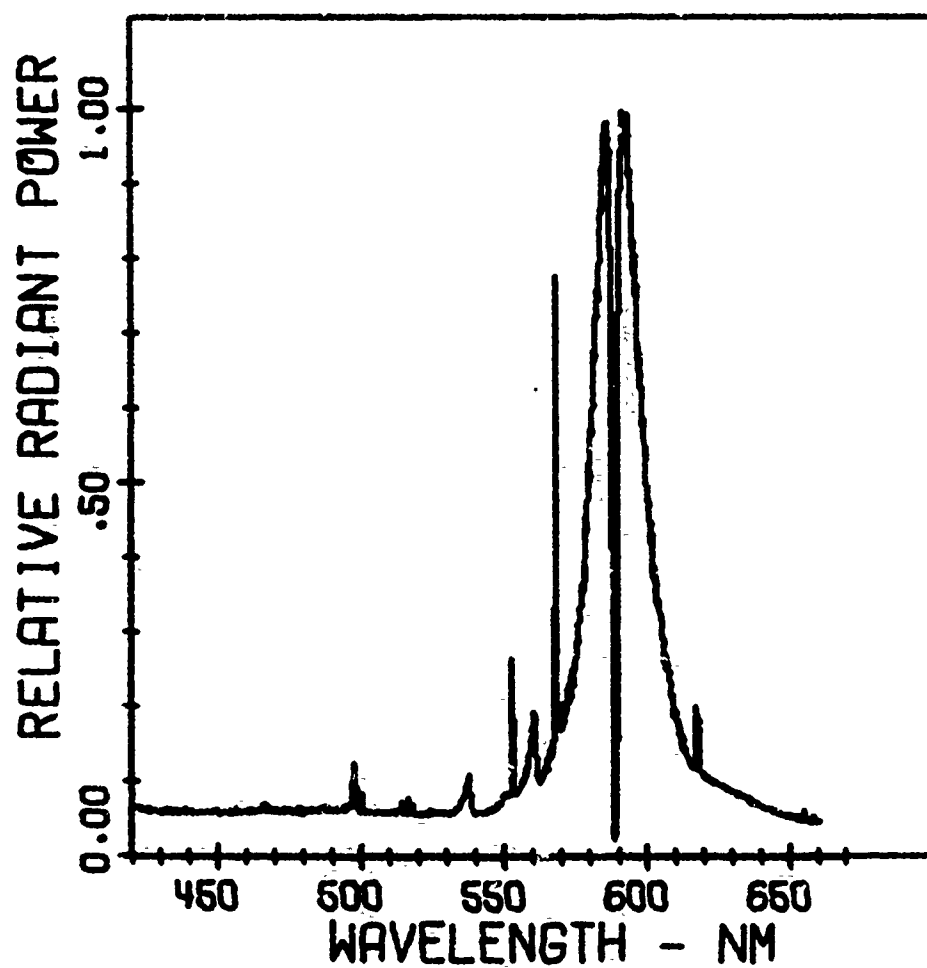


FIGURE 1. Group 101

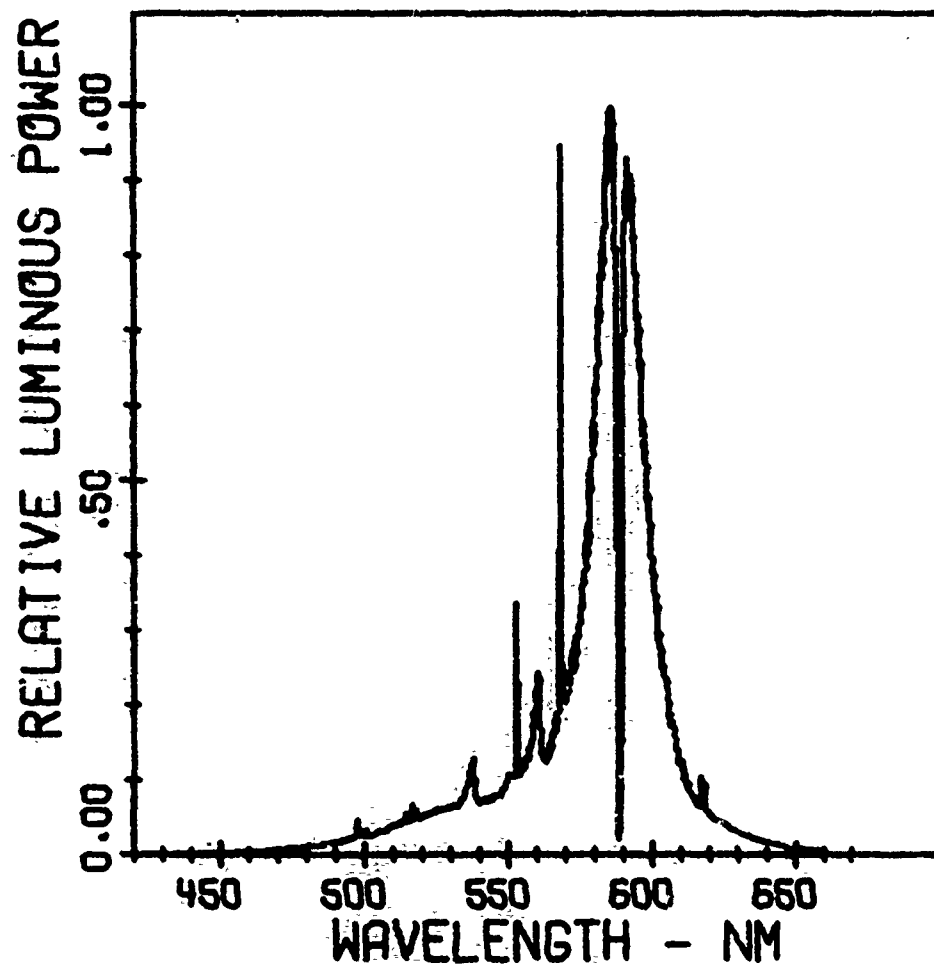


FIGURE 2. Group 101

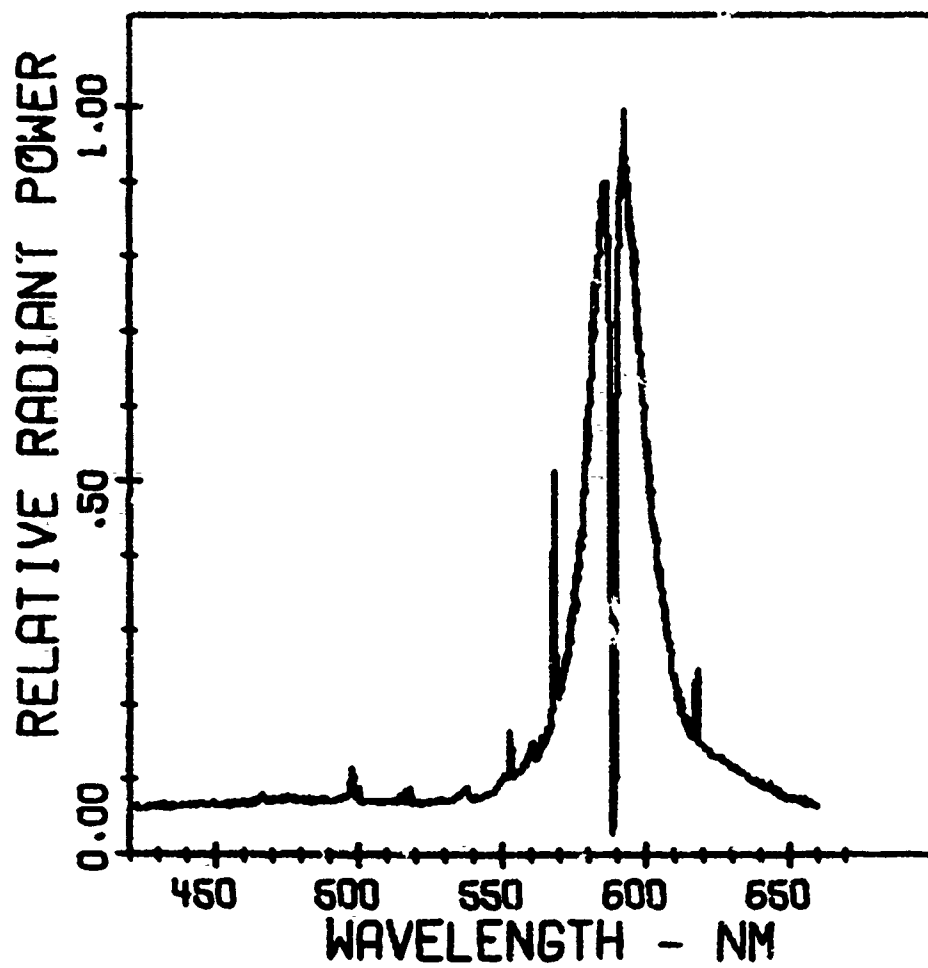


FIGURE 3. Group 102

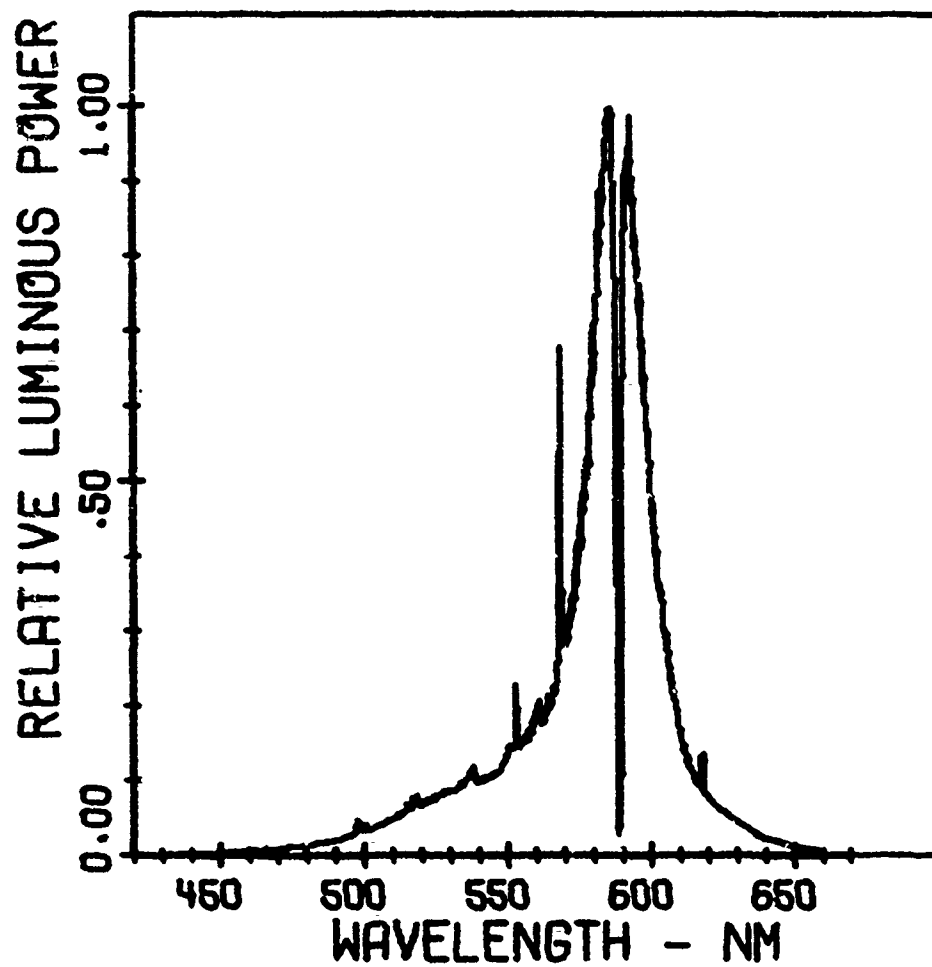


FIGURE 4. Group 102

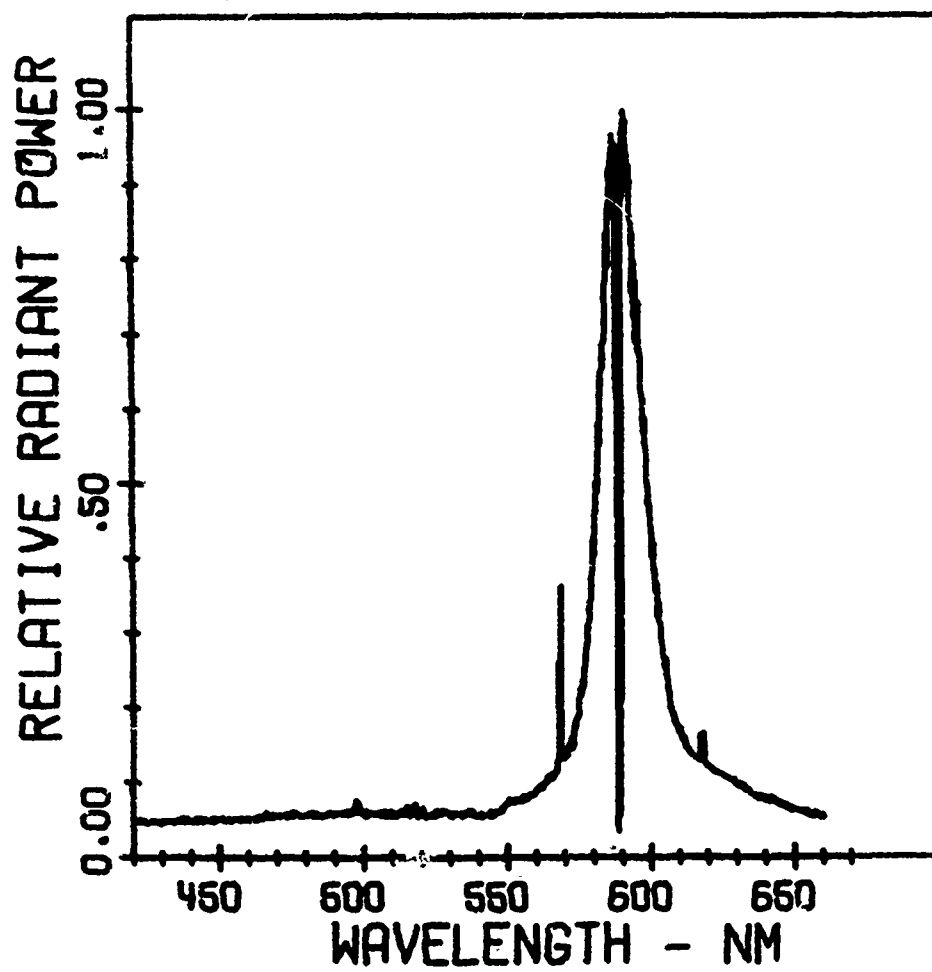


FIGURE 5. Group 103



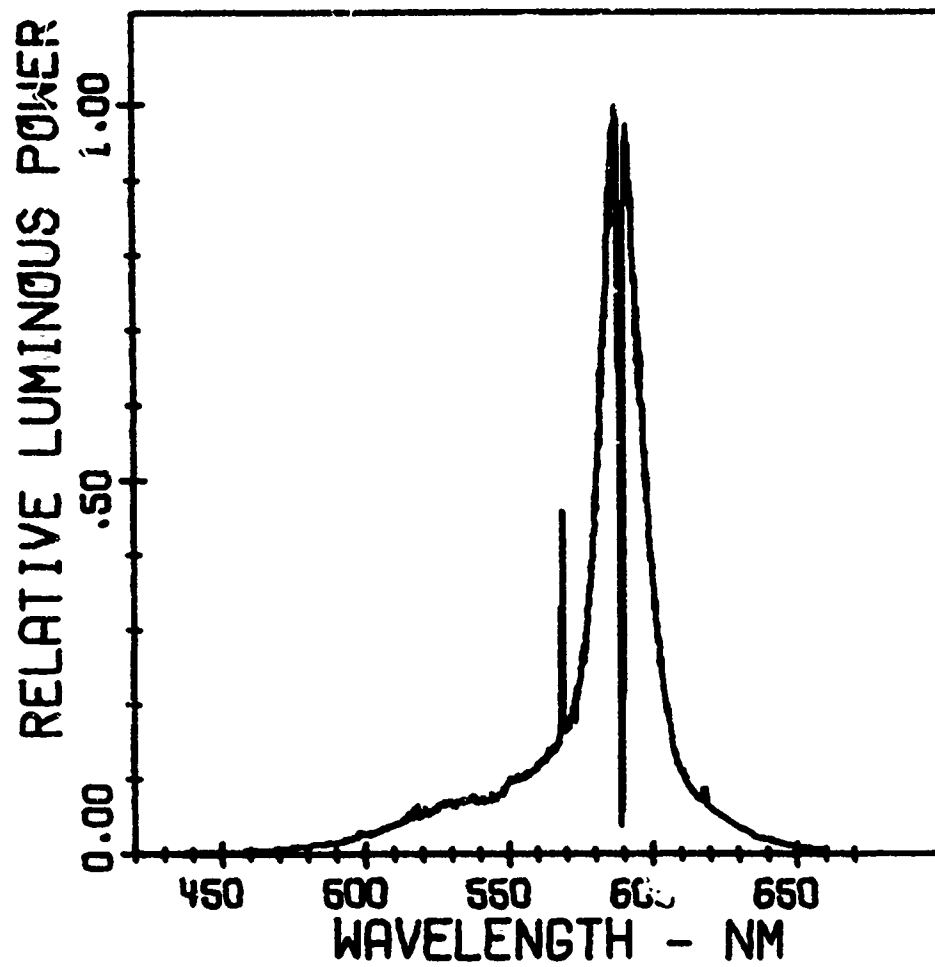


FIGURE 6. Group 103

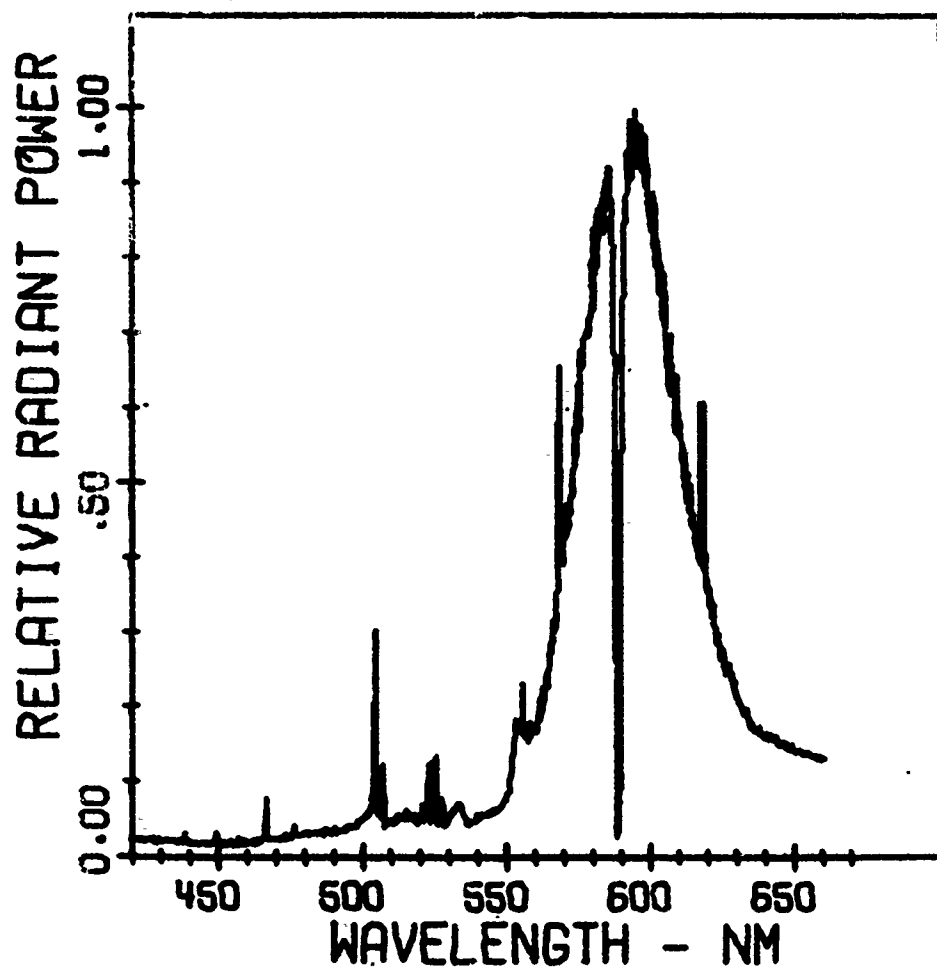


FIGURE 7. Group 104

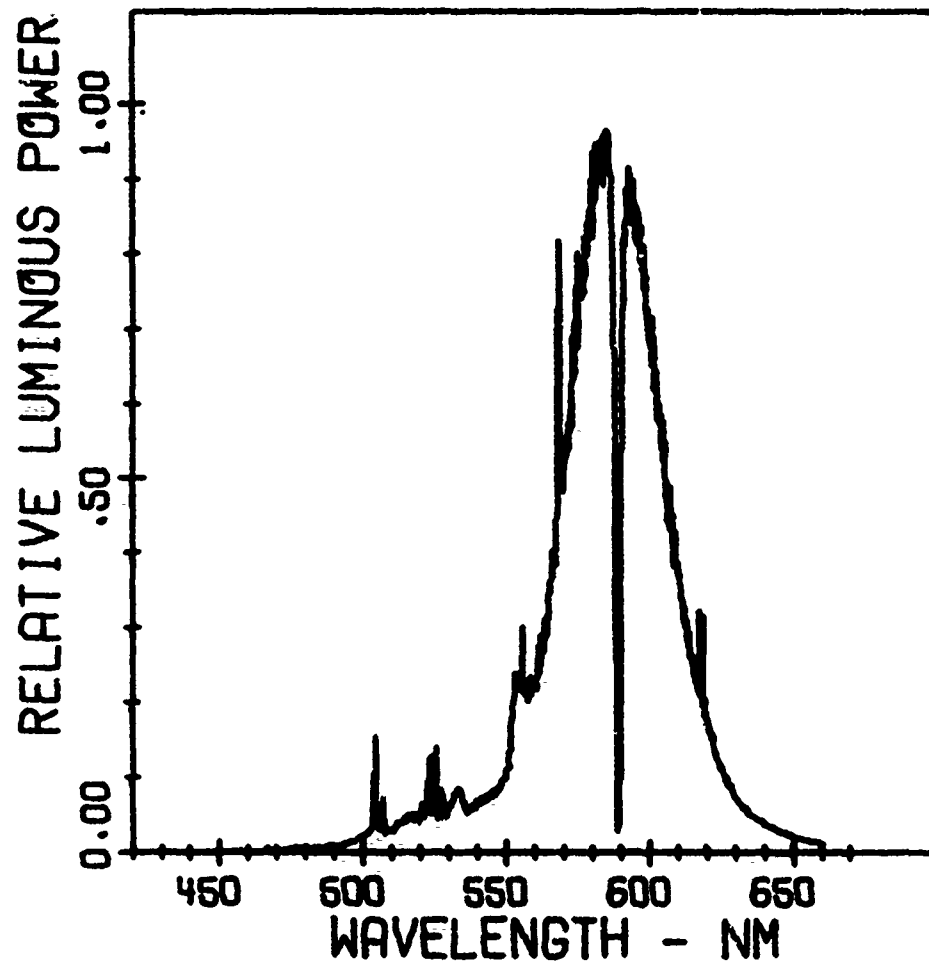


FIGURE 8. Group 104

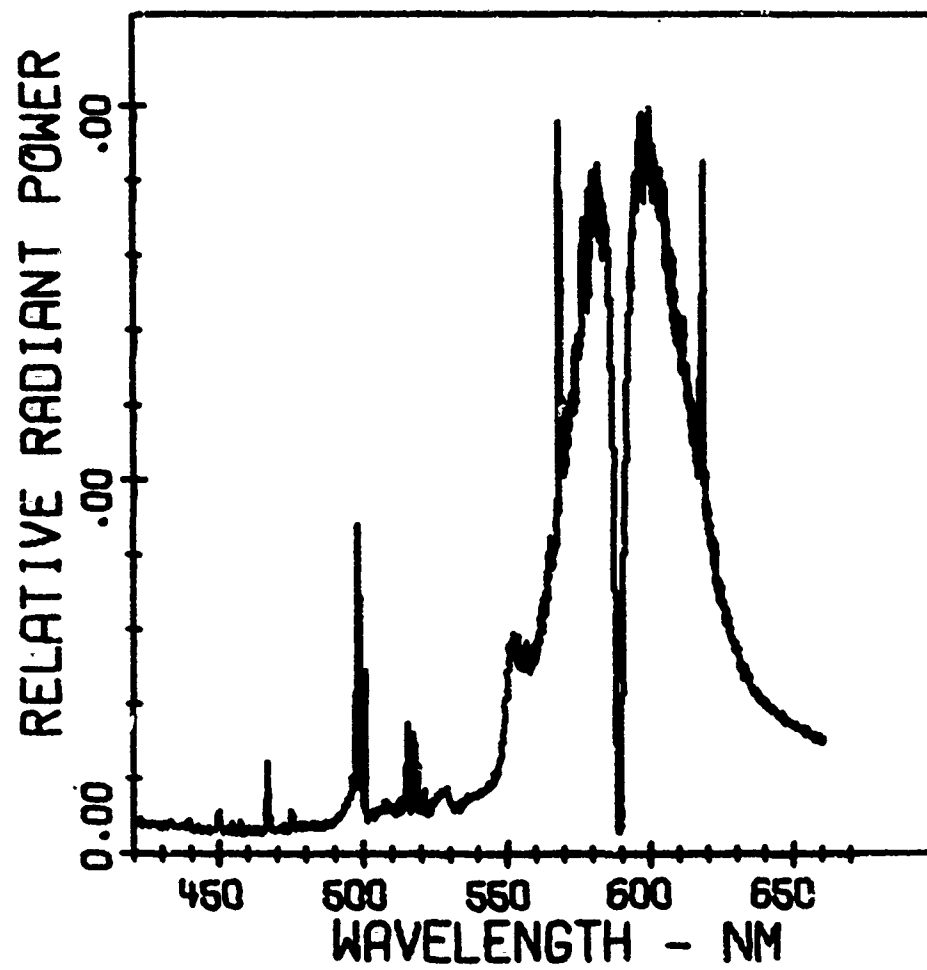


FIGURE 9. Group 105

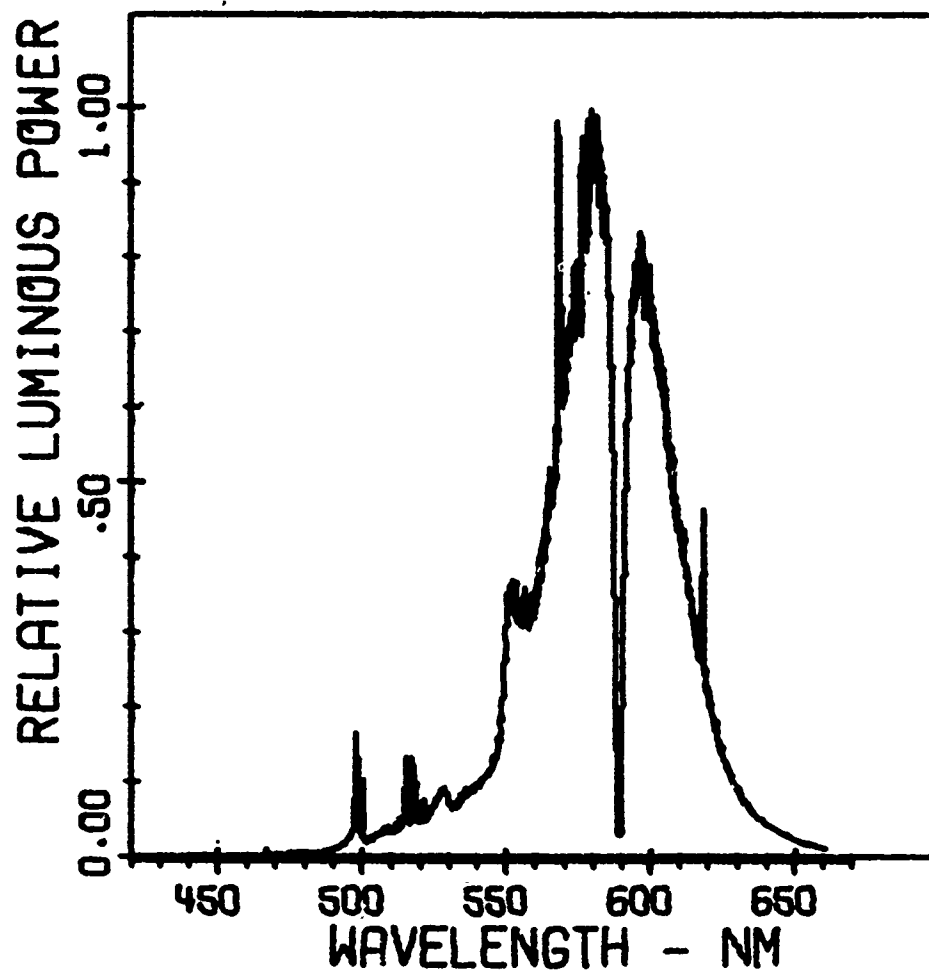


FIGURE 10. Group 105

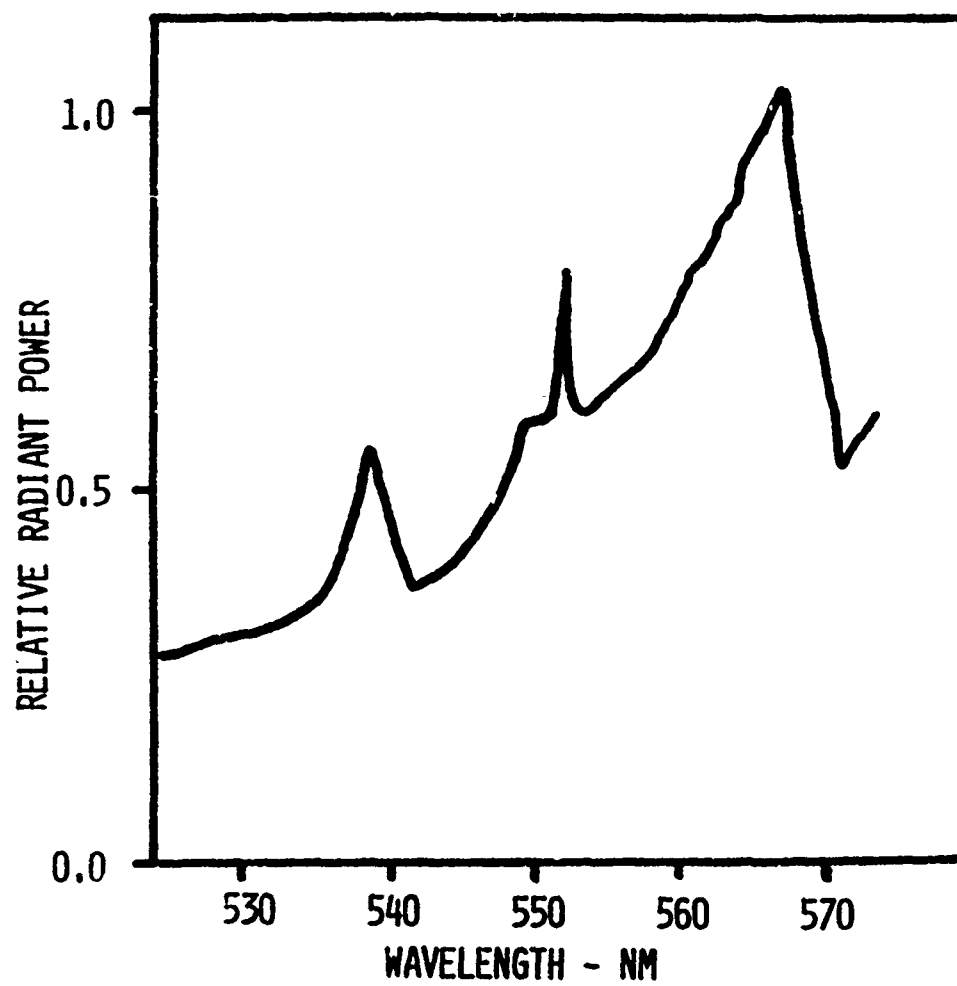


FIGURE 11. Group 101 - High Resolution

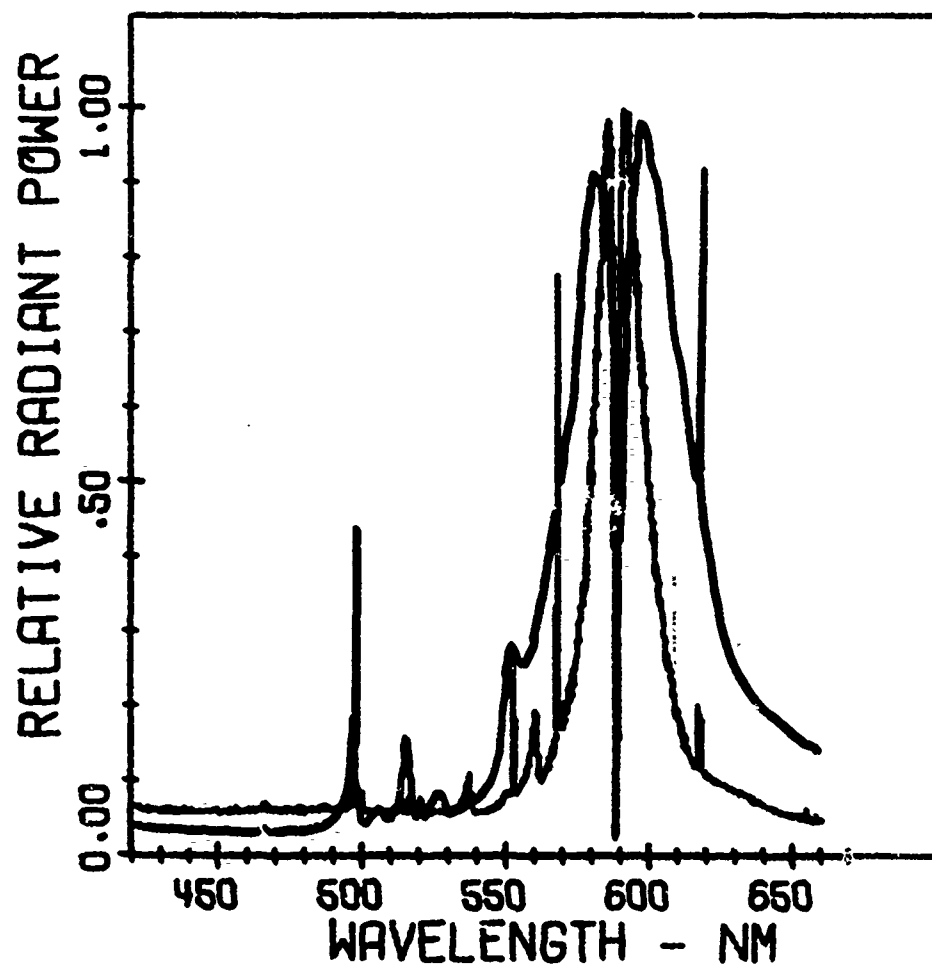


FIGURE 12. Comparison of broadening between 101 and 105

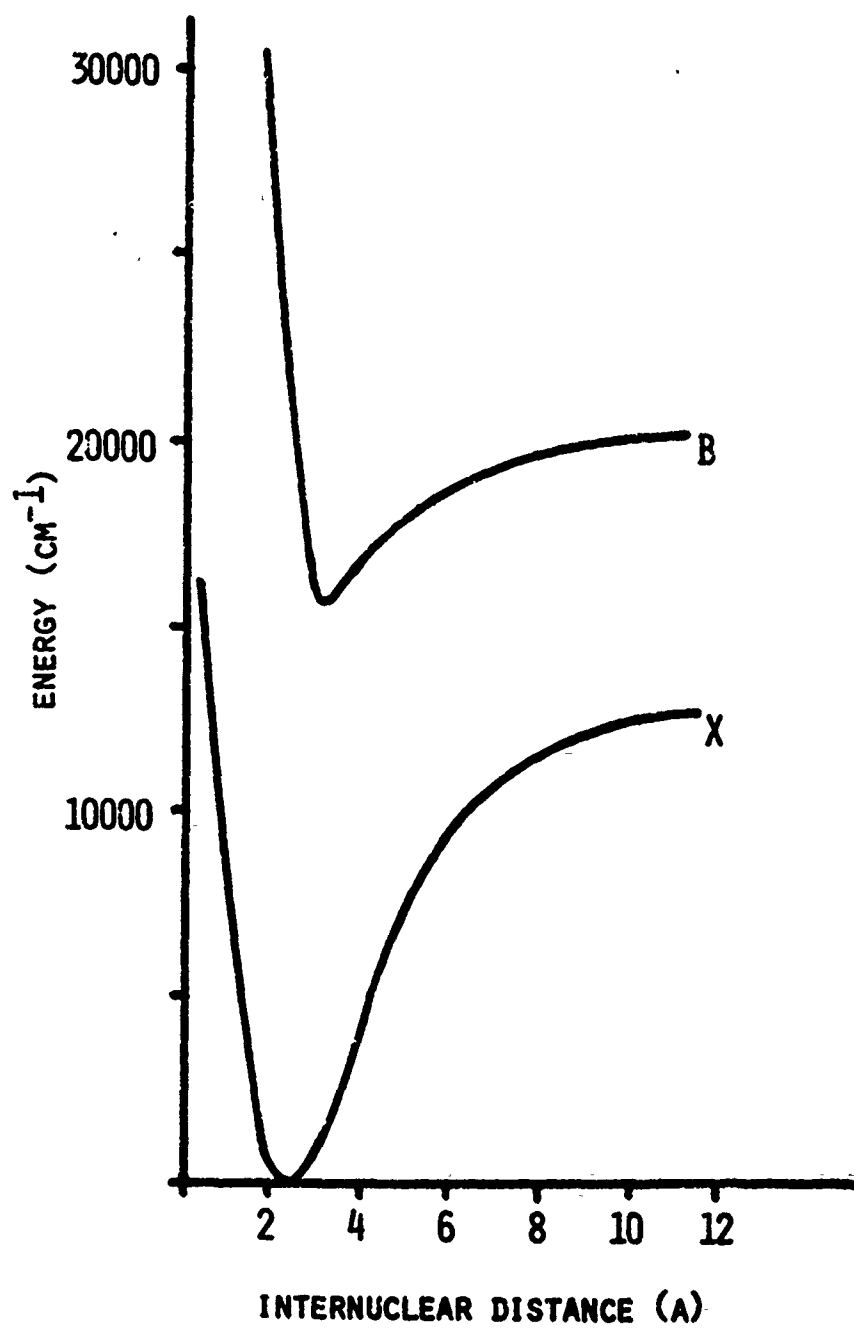


FIGURE 13. Iodine Potential Energy Surfaces



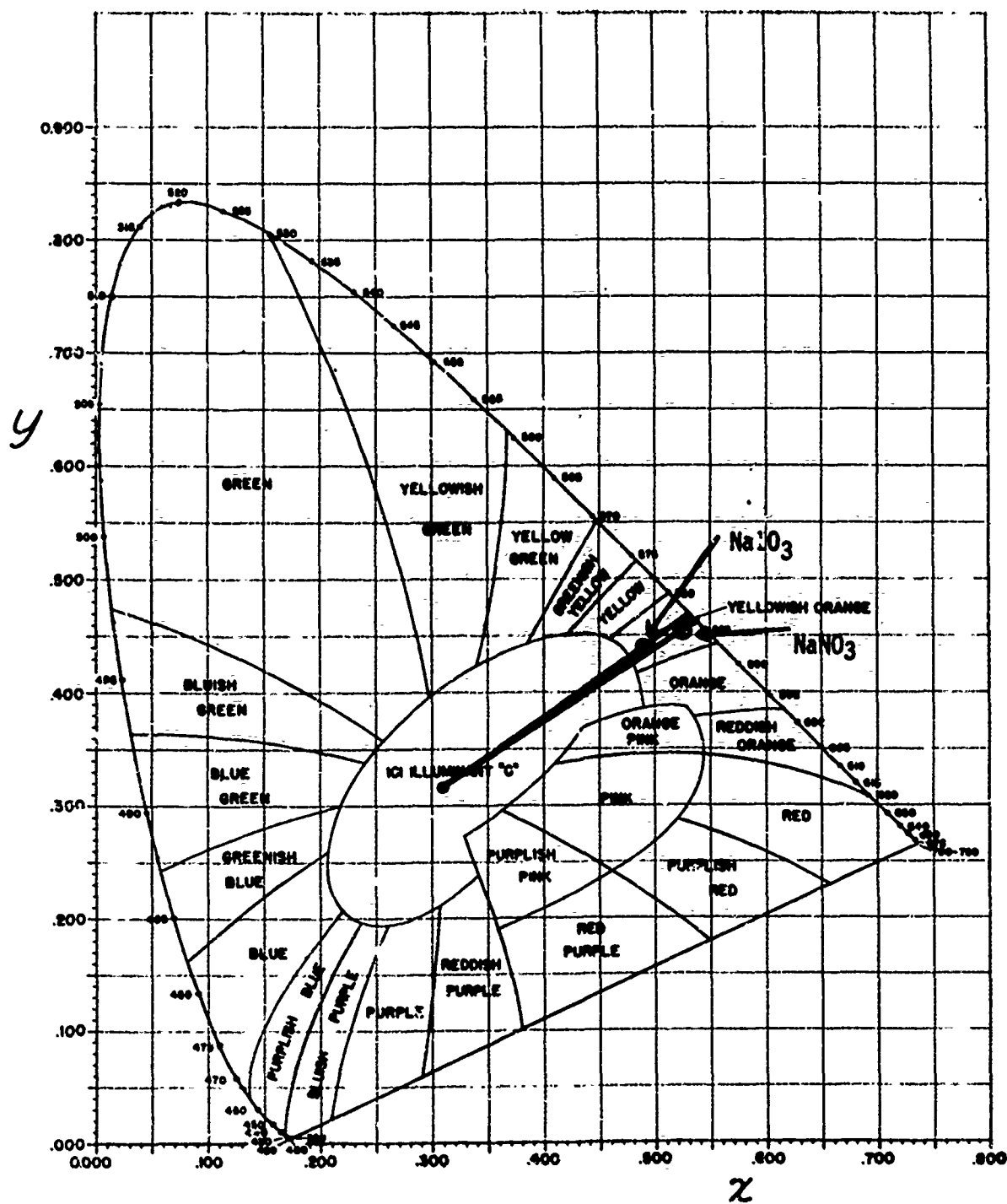


FIGURE 14. Chromaticity Diagram - Comparison of Color of 101 and 104.